

FINAL TECHNICAL REPORT

**AASERT 96 - SYNTHESIS AND PROPERTIES OF POLYARYLENE VINYLENES
FOR LED APPLICATION**

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August 1, 1996 - July 31, 1999

November 1, 1999

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ABSTRACT

Conjugated/non-conjugated alternating block copolymers containing cyano-modified distyrylbenzene units as emitting chromophores were synthesized via Knoevenagel and Wittig reactions; the non-conjugated block was an alkylene spacer. The polymers were differentiated with respect to the location of the cyano groups in the chromophoric block (double bond or phenylene ring). When photoluminescence and electroluminescence spectra of these materials were compared with those of a similar structure without the cyano group, a strong bathochromic effect was observed. A more pronounced red shift and a higher electroluminescence efficiency was observed in the polymer with the cyano group attached to the aromatic ring. These materials show promise for device manufacture.

The use of polymer based materials in light-emitting diodes (LEDs) has brought the synthesis of numerous polymer structures containing PPV-related chromophores as main-chain, side-chain or combined main- and side-chain attached groups.

Color tuning can be accomplished by several means, including substitution in the chromophore with appropriate choice of electron donor or acceptor groups, since these changes will affect the band gap. To obtain high efficiency in electroluminescence it is also necessary to match the closest possible positive and negative charge injection into the device. It has been typically found that electron injection is more difficult than hole injection and this has led to the use of low work function cathode metals such as calcium, unstable under atmospheric conditions. Polymers with intrinsically high electron affinity are therefore highly desirable, since they reduce the barrier for electron injection. Substitution with electron withdrawing groups such as cyano increases the electron affinity of the emitting layer chromophore, thus making possible the use of more stable electrodes such as aluminum.

Cyano-substituted PPV structures have been developed in which the cyano group is attached to the vinylene moiety and alkoxy groups (such as OC_6H_{13}) are substituents to the phenyl ring to provide solubility. The synthesis, the theoretical investigations of the effect of derivatization, the effects of the inclusion of alkoxy-substituted thiophene groups in the repeating unit or replacing the phenyl ring, the emission mechanism in solution and in the solid state using time resolved spectroscopy, and the effects of the substitution on chain packing and optical properties of 2,5 alkoxy substituted cyano PPV's have all been studied.

We have synthesized a new class of cyano-substituted light emitting polymers, in which the chromophores are isolated from each other through a flexible non-conjugated spacer. We have used this strategy previously in many cases. Copolymerization improves polymer solubility in organic solvents and decreases crystallinity, enhancing the properties of the film formed from spin coating or self assembling related processes. It is also a convenient way to confine conjugation, increasing the band gap and generating a blue-shifted emission spectrum. In general, compounds with relatively shorter conjugation lengths have higher photoluminescence quantum yields, producing higher electroluminescent quantum yields. Copolymerization also brings about molecular dilution of the emitting centers, decreasing self-quenching probabilities.

In the copolymers described below the cyano groups are attached either to the vinylene group (Copolymer II) or to phenyl ring (Copolymer III), as shown in Figure 1. A non-cyano substituted reference structure was also prepared for comparison. Copolymers II and III were synthesized using the Knoevenagel and Wittig routes respectively. Copolymer III is the first light-emitting polymer with a cyano group attached to the phenyl ring reported so far.

Experimental

Chloroform and tetrahydrofuran were refluxed over 4,4'-Methylenabis(phenyl isocyanate) (MDI) and distilled prior to use. Methanol was dried with molecular sieves and distilled prior to use. 1,4-Phenylenediacetonitrile, 4-dimethylaminopyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,3-dicyclohexylcarbodiimide (DCC), 2,5-dibromo-1,4-dimethylbenzene and triphenylphosphine were purchased from Aldrich and were

used without further purification. All others reagents and solvents from commercial sources were used as received.

FTIR spectra were recorded on an IBM IR3x type 913X spectrometer equipped with Nicolet PC/IR operation software. Cast films obtained from evaporation of polymer solutions in chloroform over a KBr cell were used for this purpose. ^1H and ^{13}C -NMR spectra of CDCl_3 solutions were taken on a Varian DPX300 spectrometer. GPC measurements were taken in a system composed of a WATERS 500 Pump, injector U6K, a WATERS 410 Differential Refraction Index detector, and a series of three Ultrastyrigel columns with a porosity of 10^4 , 10^3 and 10^2\AA and calibrated against polystyrene standards. THF solutions of the polymer samples were filtered through a Millipore membrane with a porosity of $0.45\text{ }\mu\text{m}$ just before injection. The elemental analysis was performed by the University of Massachusetts at Amherst Microanalytical Laboratory. Thermal transitions were determined using a Perkin Elmer DSC-7 series differential scanning calorimeter. Solid state absorption spectra were taken using a UV/Vis Perkin Elmer Lambda 9 UV/VIS/NIR spectrometer and solid state photoluminescence spectra were taken using a Perkin Elmer LS50B Luminescence Spectrometer. Thin films used for spectroscopic measurements were obtained from casting polymer solutions at a concentration of 10^{-4} M onto quartz windows.

Chloroform solutions of the polymer samples, at a concentration of 20mg/ml , were filtered through a Millipore membrane with a pore size of 0.2 nm . The solutions obtained were spin cast onto commercial ITO electrodes forming films with $80\text{-}90\text{ nm}$ thick. After evaporation a thin calcium layer was vacuum deposited over the substrate at a pressure

below 10^{-7} torr, and aluminum was subsequently deposited the same way in order to prevent the anode from oxidation and improve the mechanical integrity of the device for the measurements. All the device preparation and measurements were performed under dry argon in a dry box.

The dialdehyde 1,8-bis(4-formyl-3,5-dimethoxyphenyleneoxy)octan and 2,5-bis(bromomethyl)-1,4-dicyanobenzene were synthesized according to literature procedures.

Results and Discussion

Polymer synthesis

Scheme 1 shows the synthetic routes used to produce the polymers with cyano groups in the chromophoric block. Copolymer I which has been previously synthesized in our laboratories represents the reference structure for comparison with the new polymers.

Two different approaches were employed to obtain Copolymer II. In the first (Method II A) a Knoevenagel-type condensation was used in the conditions commonly reported that is, a strong base is used in a mixture of solvents at 50°C . Thus, sodium methoxide in a 1:1 v/v mixture of methanol and tetrahydrofuran at 25°C was used. Under these conditions crosslinking occurred during the reaction and/or the purification. This is discussed below. Moreover, it was noted that the molecular weight increased on aging, in solution or in the solid state, and some insoluble material was observed during subsequent solubilization. These results were attributed to a Michael-type addition between active methylene end groups and the vinylene groups in the polymer, since the effect was observed even in samples stored in the dark under inert atmosphere and

refrigeration. This effect was not found in the results reported for this type of reaction and can be explained by the steric hindrance provided by bulky ortho substituents in the aromatic ring, which were necessary for solubilization since the polymers were fully conjugated. These findings prompted us to use milder conditions to obtain Copolymer II.

Method B was based on very mild polycondensation conditions. The reaction was carried out in tetrahydrofuran at room temperature and promoted by 4-dimethylaminopyridine (DMAP) as a base and 1,3-dicyclohexylcarbodiimide as a condensing agent. The increase in molecular weight was followed by SEC as the reaction proceeded. After 14 hours at room temperature, a clean-cut peak appeared in the region corresponding to the molecular weight of 8,000-14,000 g/mol. After purification it was shown by $^1\text{H-NMR}$ that no side reactions took place to any significant extent. Polymers obtained using this method showed good photoluminescence spectra reproducibility. The improved performance of this method can be explained by the fact that DCC may halt the condensation reaction during aldol formation, due to the possibility of an adduct formation, thus leading to undesirable Michael additions. At the end of the polymerization reaction any adduct formed between DCC and the aldol function was, if necessary, destroyed by a gentle reflux of the reaction mixture.

The Wittig-type polycondensation, used to synthesize Copolymer III, was easily accomplished by the reaction between the dialdehyde and the ylide, which was formed *in situ* from the reaction between 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and the corresponding phosphonium salt. A polymer with molecular weight of 6,000 g/mol was obtained in a few hours at room temperature. The polymer was isomerized to all-trans

configuration by refluxing the polymer solution in toluene with a catalytic amount of iodine.

The Wittig polymerization carries advantages over the Knoevenagel polymerization, since in the former there is no possibility of crosslinking reactions, and as a result the probability of structural defects is lower. The Wittig reaction is favored by the enhanced acidity of the methylenic protons of the phosphonium salt, caused by the presence of the two electron withdrawing cyano groups. Consequently, weaker bases, such as tertiary amines, can be used to promote ylide formation without affecting the cyano and aldehyde groups, both of which are sensitive to strong basic media. This is therefore a good synthetic strategy for the production of cyano-containing PPV-like structures.

ii. Structural and thermal characterization of the polymers

The molecular weight of the Knoevenagel polycondensation polymers was controlled by the reaction time or by the polymer solubility. The two Wittig polycondensation polymers, Copolymers I and III showed quite different molecular weights. This can be attributed to the difference in monomer reactivity, since the polymer with the lower molecular weight resulted from the less reactive cyano-substituted ylide which seemed to be relatively stable, even in the presence of a small amount of protic solvent added to the reaction medium.

DSC curves of the polymer samples showed only second order transitions, characterized as the T_g transitions, during heating steps at a 20°C/min. No apparent crystallization was observed after annealing the samples above their T_g for 24 hours. The somewhat low values of these transitions are associated with the thermal motion of

the alkylene soft blocks. The T_g values increased with increasing molecular weight and it may be that the molecular weight of Copolymer **II-A** lies between those of Copolymer **I** and Copolymer **II-B**.

Method A produces a polymer with some structural defects, as indicated by the presence of multiple peaks observed in the $1690\text{--}1710\text{ cm}^{-1}$ FTIR region. They can be assigned to carboxylic groups produced by hydrolysis of the cyano groups or by a Cannizzaro reaction of the aldehyde terminal groups promoted by the strong basic conditions used in this method.

(iii) Absorption and photoluminescence properties

The solid state photoluminescent spectra of the copolymers were obtained from solid thin films cast onto glass plates and with excitation at 390 nm. Copolymer **I** showed a characteristic blue emission at 453 nm. The introduction of the cyano groups into this structure brought about a large bathochromic effect. Copolymer **II** emitted at 497 nm, while Copolymer **III** showed a greenish-yellow emission at 533 nm. Solutions of this copolymer in apolar solvents are visibly fluorescent even when observed in a brightly lit room.

The energy level of the conduction band is lowered by increasing the electron affinity of the polymer, and since cyano groups lower the LUMO energy, a corresponding shift of the emission towards longer wavelengths is expected. In the case of poly(cyanoterephthalylidene)s the LUMO band is lowered by 0.9 eV and the HOMO band by 0.6 eV relative to PPV, causing the emission to change from greenish yellow to red.

Another feature of Copolymers **II** and **III** is the presence of methoxy electron

donating groups, which induce strong permanent dipoles affecting the donor/acceptor strengths of the OCH_3 and CN groups. These dipoles increase the electron density in the chromophoric block and consequently bring about a decrease of the energy of the excited state. Therefore the relaxational decay produces lower frequency emission. In fact, the absorption spectra of the cyano-based polymers showed a $\pi\text{-}\pi^*$ transition at lower frequencies than Copolymer I. This effect is more pronounced in Copolymer III where the two methoxy substituents and the two electron withdrawing CN substituents are attached to separate aromatic rings. Moreover, the CN groups are one π system away in relation to Copolymer II. This difference in electron density is reflected in different chemical shifts in the NMR.

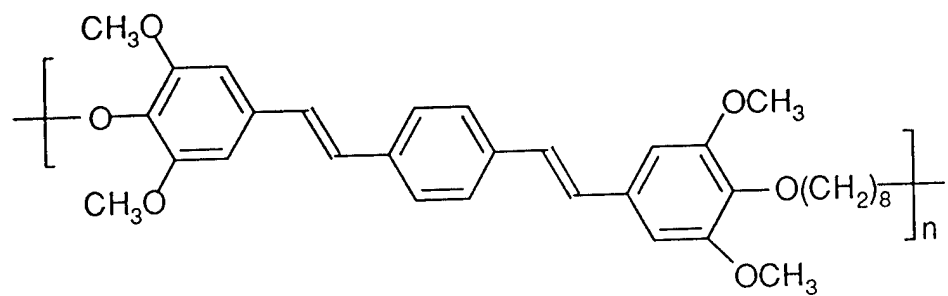
In Copolymer III the effect of charge delocalization is much higher than in Copolymer II.

(iv) Electroluminescent properties

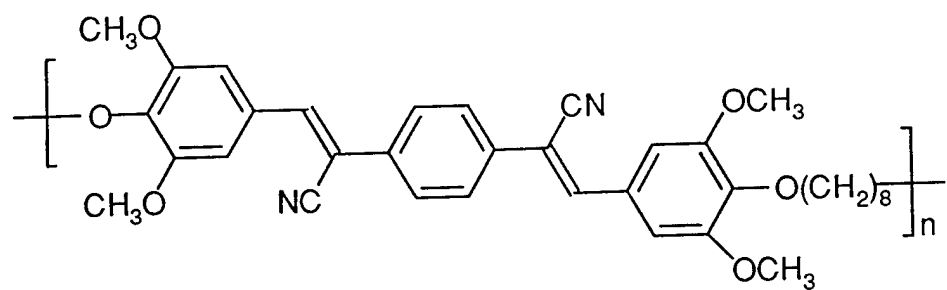
The intensities of the EL spectra were normalized in order to facilitate comparison of the emission properties of each sample. The EL spectra of all samples were wider and slightly red-shifted in relation to the corresponding solid state PL spectra. This is probably due to interactions between the chromophores and ITO at the interface polymer-electrode. In fact, PL spectra taken directly from the devices were consistent with the respective EL spectra. Copolymer II showed a low intensity emission, centered at 505 nm. The Copolymer III device showed good performance and a yellow emission centered at 553 nm could be observed in a well lit room. At a 13 V applied forward bias the device turns on, and the current function showed a close relation with the output emission

intensity. This indicates a highly balanced charge injection and a facile charge recombination.

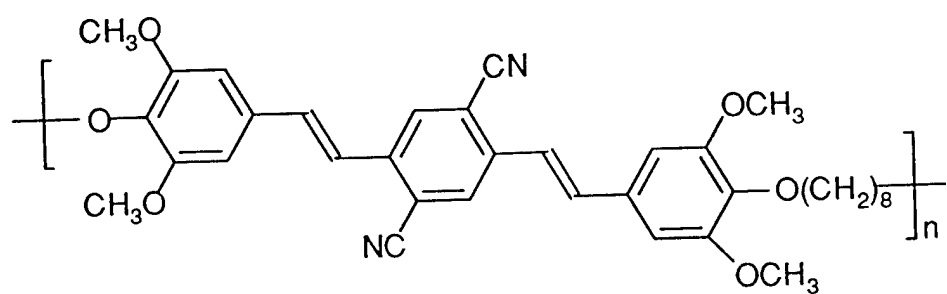
Thus these block copolymers containing a methylene based spacer and cyano substituted PPV segments were prepared for the first time. The cyano groups were located in the vinylidene bond (Copolymer II) or in the aromatic ring (Copolymer III). Copolymer II was prepared via a Knoevenagel route and Copolymer III was made using a Wittig reaction. The latter process afforded a more perfect structure, whereas there was a possibility of side reactions in the former. The PL and EL spectra of the new polymers showed a red shift in relation to the non-substituted copolymer. This was attributed to the increase in the electron dispersion brought about by the enhanced polarization. Copolymer II showed a bright yellow EL emission centered at 558 nm.



Copolymer I



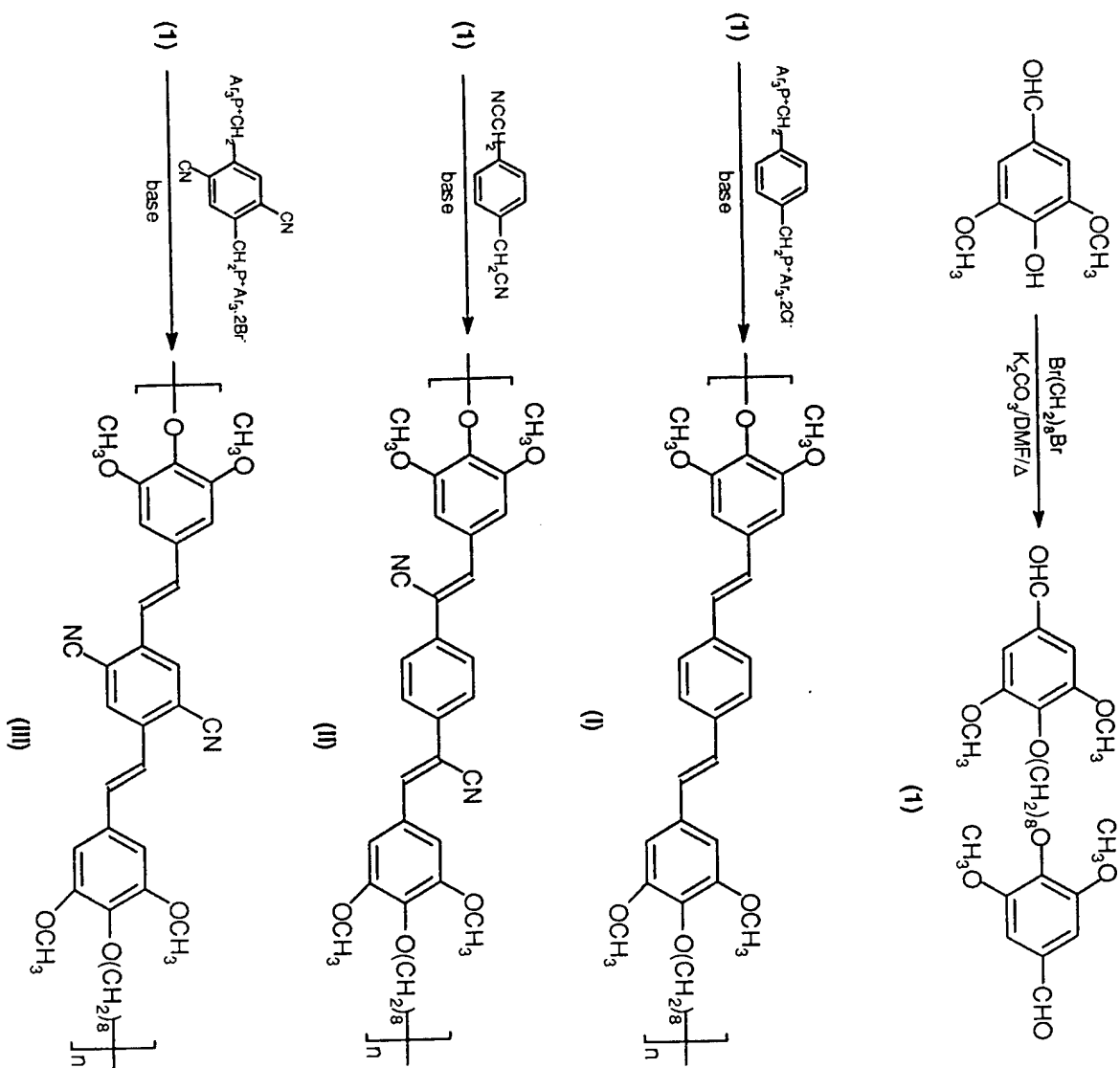
Copolymer II



Copolymer III

Figure 1

Scheme 1:



COMPLETED PROJECT SUMMARY

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PUBLICATIONS (Partially or fully supported by this grant)

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